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SOLAR FLAT PLATE THERMOELECTRIC GENERATOR RESEARCH

15 JUNE 1963

QUARTERLY REPORT NUMBER 1

FOR THE PERIOD

1 MARCH 1963 TO 1 JUNE 1963

FLIGHT ACCESSORIES LABORATORY

AERONAUTICAL SYSTEMS DIVISION

WRIGHT PATTERSON AIR FORCE BASE, OHIO

PROJECT NUMBER: 8173

TASK NUMBER: 817302

PREPARED UNDER CONTRACT AF33(657)-10335

BY GENERAL INSTRUMENT CORPORATION

THERMOELECTRIC DIVISION

NEWARK, NEW JERSEY

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ABSTRACT

A solar flat plate thermoelectric generator consists of a collector plate with an optically selective coating, small size semiconductor thermoelements, a radiator plate and a support structure. This report describes three months of research and development work on this space auxiliary power system.

The technical problem areas investigated include; collector coatings, thermoelectric materials and contacts and support structures. Collector coating samples suitable for evaluation have been obtained from one supplier. Test equipment for thermal cycling tests of solar thermoelectric panels has been fabricated. Panels using a plastic foam support structure and on aluminum honeycomb support structure have been fabricated and tested. A number of different thermoelectric materials have been tested for efficiency at various operating temperatures.

FOREWORD

The work covered by this report was accomplished under Air Force Contract AF33(657)-10335, Aeronautical Systems Division, Aero Propulsion Laboratory, C. W. Glassburn, Project Engineer/ASRPP-20. This report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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I. INTRODUCTION

Potential advantages in reliability and weight compared to existing and most projected space power sources has led to a continuing interest in the solar flat plate thermoelectric concept. This interest has arisen despite a low efficiency and the consequent need for large arrays of panels, if significant amounts of power are needed. However, in addition to the high power to weight ratio this system will be virtually impervious to the environment of space, i.e., vacuum, zero gravity, Van Allen radiation, solar flares, meteorites, etc. The solar tracking problem is minimized since the output should vary as the sine of the orientation error. Thus, a system employing this concept has the potentiality of being the only space vehicle auxiliary power supply that does not employ an expensive nuclear heat source, does not require extremely accurate solar tracking and yet will have exceptionally low overall weight and cost and a very high inherent reliability.

An optimization study, relating to optical coatings, thermoelectric materials and operating temperatures has been performed to establish required design criteria*. This study clearly illuminated the necessity of basing system design upon established state-of-the-art both in collector coatings and in thermoelectric materials. Much of the initial effort in this program has thus been devoted to establishing a precise definition of the existing state-of-art rather than in any attempt to search for radical "break throughs".

The most significant design engineering problems in this program lie in the areas of intra-panel and inter-panel support structures. The work performed to date has concentrated on intra-plate support structure design and test.

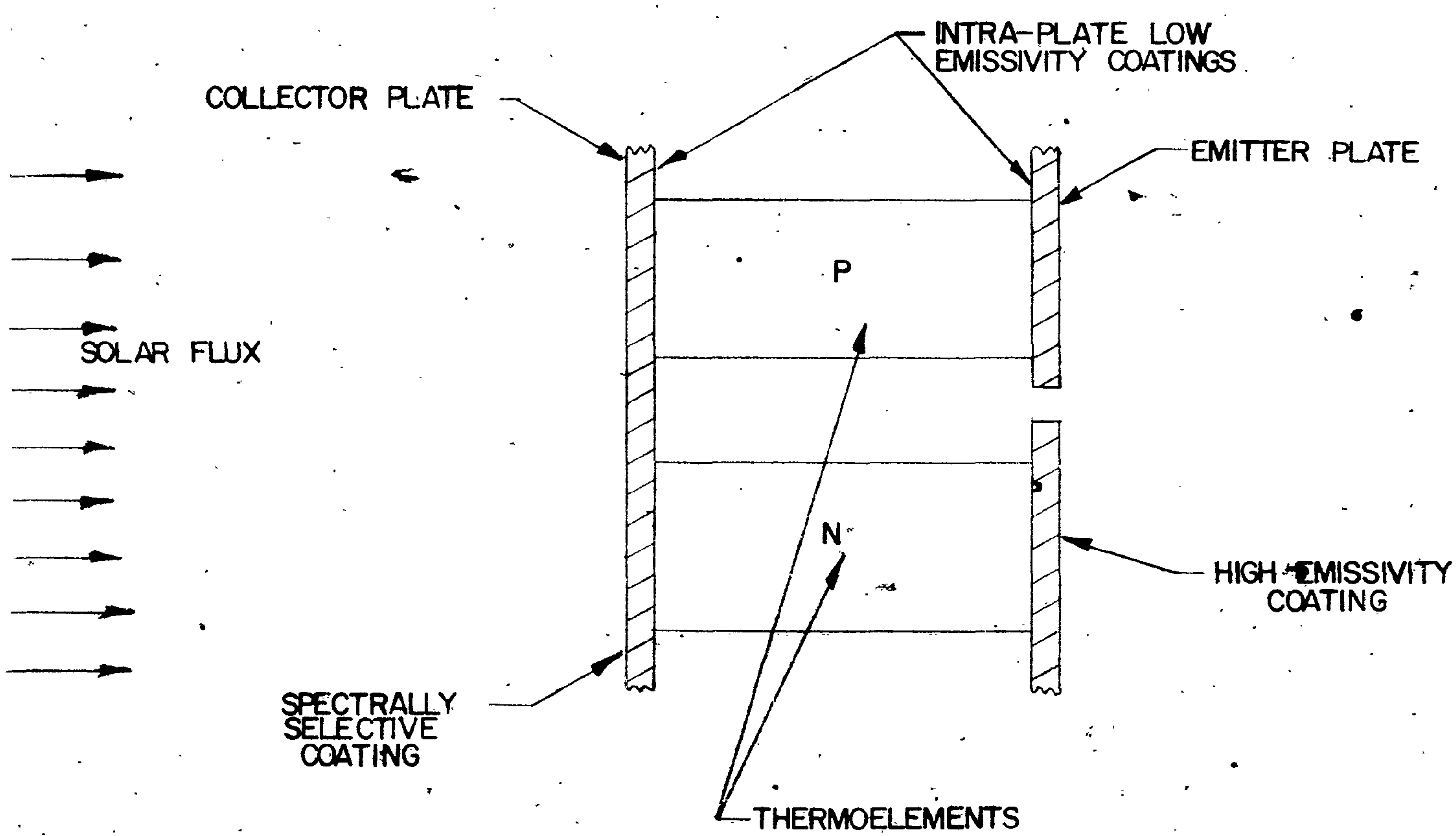
* Proposal, KN-142, General Instrument Corp. to USAF

II. SYSTEM DESCRIPTION

The solar flat plate thermoelectric generator concept is shown, in its simplest form in Figure II-1. In addition to the components called out in that figure provision must be made for intra-panel and inter-panel support structures. These structural members are required for handling, deployment and orientation.

Of the incoming solar energy some portion is reflected, depending on the absorptance of the collector in the visual portion of the spectrum. Another portion is re-radiated from the collector depending on the infra-red emissivity of the collector and the collector temperature. The remaining portion of the incoming energy, less that amount lost by direct radiation from the collector to the radiator plate, passes through the thermoelements and is available for conversion to electricity. The conversion efficiency is dependent upon the collector temperature, the radiator temperature, and the thermoelectric properties of the thermoelements which are themselves temperature dependent.

In order to minimize damage due to micro meteorite penetration it is necessary to use a number of small size thermoelements in parallel for each "leg" of each thermocouple.



CONCEPTUAL SCHEMATIC OF FLAT PLATE SOLAR THERMOELECTRIC CONVERTOR

FIG. II-1

III. COLLECTOR COATING

As discussed earlier, an optical collector coating, combining high absorptivity in the visual with low emissivity in the infra-red, is essential to this system. It is imperative that data be obtained of optical properties as a function of temperature for state-of-art collector coatings in order to design an optimum system.

A program for evaluating the present state-of-art for collector coatings was developed in conjunction with ASD personnel. All known potential suppliers of this type of coating were contacted by letter inquiry with supplementary telephone contact in some cases. These potential suppliers were asked to submit quotations on evaluation samples. A typical inquiry letter is appended to this section. The results of the survey are given in Table III-1 below.

TABLE III-1

Potential Supplier	Results
Minneapolis Honeywell Research Center	Two letters plus telephone follow-up. They are presently under contract with ASD for coating development but most of their work has pointed towards higher temperatures. They have promised to give an answer in the near future.
Spectrolab Inc.	No reply to letter inquiry.
Bausch and Lomb Optical Co.	No reply to letter inquiry.
National Research Corp.	Letter inquiry plus telephone discussion. They have had no experience in this area and have no recommendation beyond an R and D program.
Optical Coating Laboratory Inc.	Submitted quotation evaluation samples on a best effort basis. Coating proposed same as Kinney. No claims of experience or test results.

Kinney Vacuum	Samples obtained and supplied to ASD for experimental evaluation.

The original intent was to obtain samples from a number of suppliers and submit these samples to ASD for evaluation. As of this time only Kinney samples appear suitable for this evaluation.

IV. THERMOELECTRIC MATERIALS

The thermoelectric elements used in a flat plate solar thermoelectric power source are of major importance in determining system performance. These elements must satisfy the following criteria; have a high thermoelectric figure-of-merit in the temperature range of interest, be capable of being joined to collector and radiator plates in a mechanically strong, electrically stable manner, possess stability with thermal cycling, not be damaged by sublimation at expected operating temperatures, be capable of being fabricated in small sizes and possess adequate mechanical strength.

At the beginning of this program a set of "ground rules" were established for this program:

1) Thermoelement Length = .25 cm
2) Thermoelement Area: .01 to .04 cm^2
3) Hot Junction Temperature: 200-230°C
4) Cold Junction Temperature: Approximately 100°C.

Several possible materials have been investigated as to their suitability for this program and are listed in Table IV-1. Of particular interest is the figure of merit, Z, in the temperature range of interest. The figure of merit has been determined using the well-known "ΔT_{max}" technique.* The test program for obtaining all the required data is still continuing.

Several difficulties have developed which have impeded the test program for determining figure of merit for the bismuth telluride microelements. Processing problems developed in the soldering of

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* Ioffe, "Semiconductor Thermoelements and Thermoelectric Cooling", Infosearch

TABLE IV-1

Description of Material	Figure of Merit, Z $°C^{-1}$	Remarks
'P' and 'N' Bismuth Telluride commercial material, grown from a melt		
7 mm diameter	1.4,100-230°C	
2 mm x 2 mm (suitable for the flat plate)	Not yet measured	High cost
'P' and 'N' bismuth telluride General Instr. Corp. pressed and sintered ingots, too large for flate plate microelements	1.4,100-230°C	
directly pressed to size	too low to be useful	
microelements, cut to size for flat plate application	not yet measured	
'P' bismuth telluride and 'N' lead telluride	not yet measured	'N' lead telluride powder on order from Minnesota Mining & Manufacturing Co.

of bismuth telluride microelements to nickel contacts and several process changes were required before satisfactory results were obtained. Another problem developed due to degradation of thermoelectric properties resulting from the cutting of bismuth telluride ingots into microelements. An investigation of this problem is currently being conducted and has not so far been satisfactorily resolved.

Two methods of joining the thermoelectric elements to the aluminum collector and radiator sheets have been considered. The first method is to electrodeposit a 0.0005" to 0.001" thick deposit of nickel on the aluminum to which the elements can be soldered. The difficulty with this technique is that if the nickel were to be deposited uniformly over the surface, it would result in an unacceptable weight penalty (a thinner deposit is not satisfactory for soldering). To selectively apply the nickel by masking is prohibitively expensive.

The second method is to electrodeposit gold on one side of each aluminum sheet at a thickness of 0.0001 to 0.00005". A nickel diffusion barrier is then soldered to each side of each thermoelement and is, in turn, soldered to the gold plated aluminum sheet. The gold also provides a low emissivity surface to reduce intra-plate radiant heat transfer. The development work in this program has utilized this second method exclusively.

V. SUPPORT STRUCTURE

A solar flat plate panel, as presently visualized, will consist of a number of separate collector sheets and a number of separate radiator sheets. These separate sheets are necessary to obtain the proper series connection of elements which is required if the panels are to have adequate voltage characteristics. In order to be able to use these very flimsy sheets, with elements sandwiched between, it is necessary to incorporate a support structure, if only for handling and erection purposes. It may also prove necessary to incorporate a support structure to provide vibration and shock resistance. "Panel support structure" is therefore defined as any feature or component included in panel design for handling ease or vibration and shock resistance

Prior to the start of this program a prototype panel, 2" x 2", had been fabricated in our laboratory using .040" x .040" x .240" thermoelements. No specific support structure was incorporated. It was of interest to determine the performance of this unit in a vibrational environment. The panel was attached to a vibration test fixture, shown in Figure V-1, and tested to the sweep frequency cps, indicated below,

Sweep Frequency (all three axes)		"G" loading
5-14		0.5" double amplitude
14-3000		5g
40-3000		7.5
400-3000	Total time of	15
40-3000	Vibration test:	15
40-3000	4 hours	20
40-3000		25
50		30 (15 minutes)

No panel damage was detected until after the final 50 cps exposure.

Examination then disclosed a partial break in a tin solder joint between a nickel contact and the collector sheet. One crack in the aluminum collector sheet and one crack in the emitter sheet was observed, in both cases these cracks were in the vicinity of a nickel contact.

These results are considered very promising, even though only a small size panel was tested, for the following reasons:

a) the "G" loading and time of the test was more severe than anticipated in actual operation.

b) the thermoelements were .240" long, whereas the elements planned for future panels are only 0.100" long. The longer element length probably resulted in larger stresses than would be encountered in an operational unit.

In the vibration table mounting fixture used in the test described above, shown in Figure V-1, the radiator sheet was firmly supported by the fixture while the collector sheets were entirely unsupported. The favorable test results indicated the possibility that a satisfactory flat plate converter could be made without reinforcing or rigidizing the collector sheets.

Two solar flat plate panels, 4" x 4" have been fabricated during the quarter. One used a plastic foam, Emerson and Cuming Eccofoam S.H. (8 pounds per cubic foot) to support the radiator sheets as illustrated in Figure V-2. The other used an aluminum honeycomb, Hexcel Corporation, (4.3 pounds per cubic foot) for radiator sheet support as illustrated in Figure V-6. A weight analysis for these panels is given in Table V-1. A detailed discussion of this weight analysis and areas for weight reduction is given below.

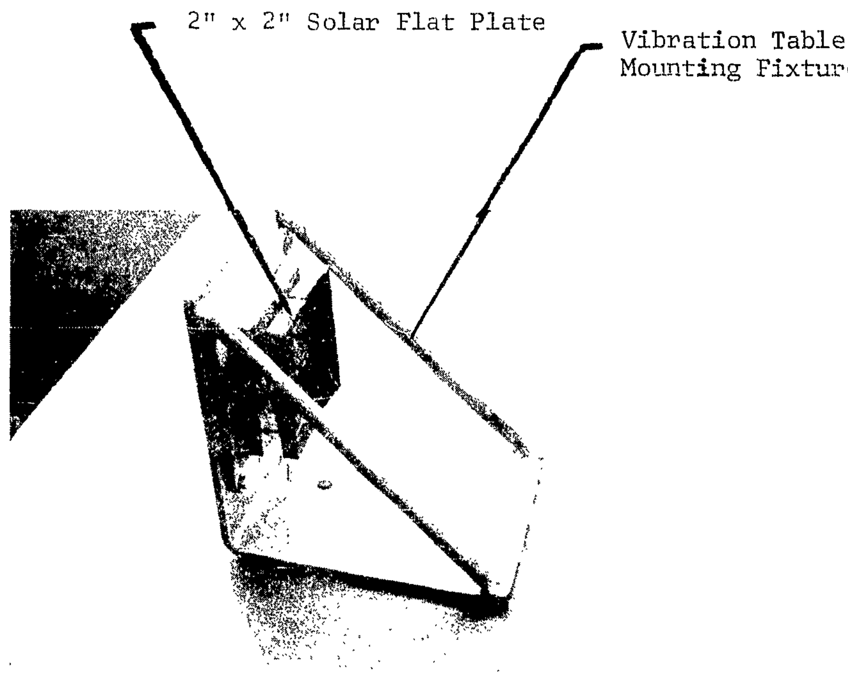
Thermocouple sub-assemblies using N and P bismuth telluride thermoelectric elements were prepared as described in Section IV. The sub-assemblies used nickel caps, 0.005" thick and 0.125" in diameter,

and .040" x .040" x 0.100" long thermoelements. These thermoelements did not have optimum thermoelectric properties because the primary purpose was structural evaluation. These sub-assemblies were bonded to 1" x 4" collector sheets using a lead/silver solder for one-half of the assemblies and a gold/tin solder for the other half. The elements were placed on 1/2" spacings. The nickel caps were then "tinned" with lead/tin solder, 350°F melting point, and attached to the radiator sheets.

The elements were arranged so that the 4" x 4" panel had four couples in series with eight elements in parallel in each leg of each thermocouple. Two of the four collector sheets were slotted between thermocouple locations for possible stress relief. See Air Force Report ASD-TDR-62-214.

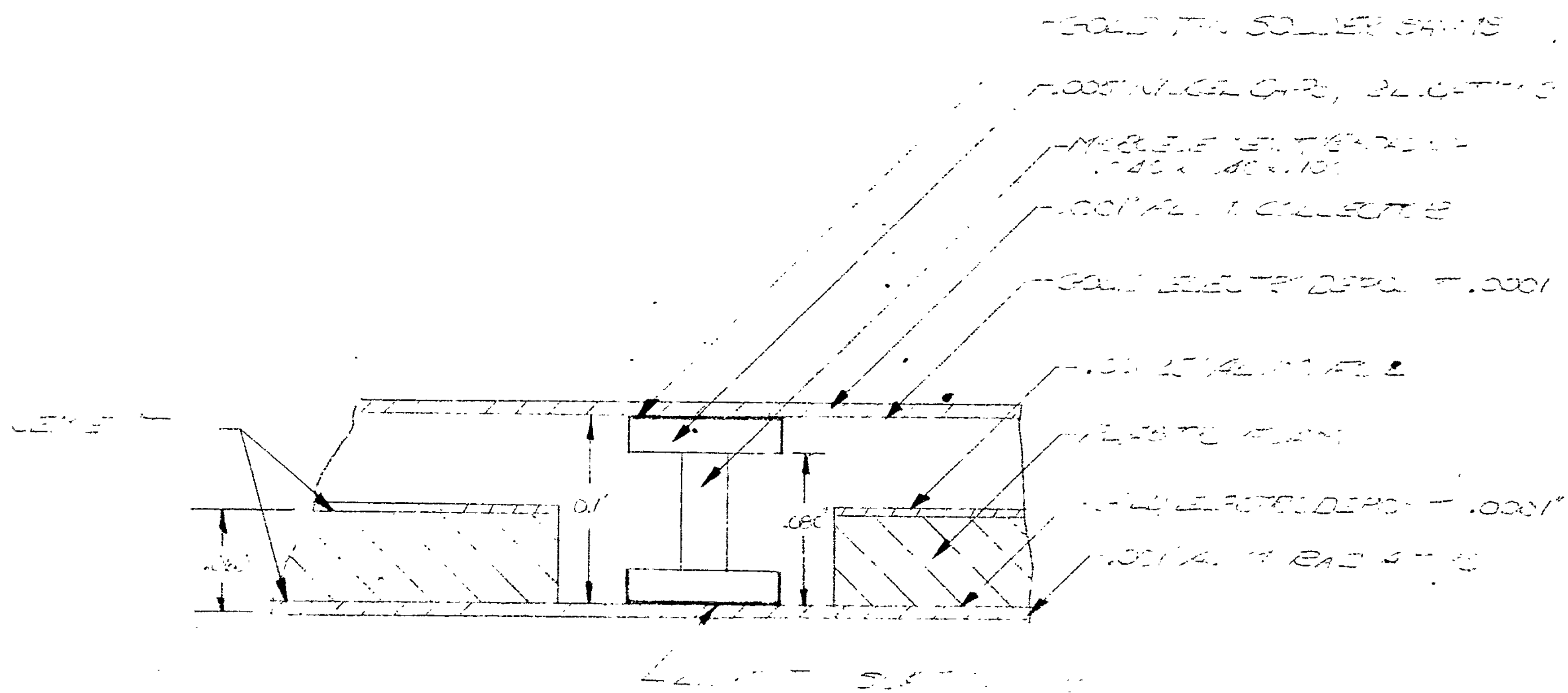
Temperature sensors, 30 gauge chromel/alumel thermocouples, were attached to the collector and radiator plates. Suitable leads of alumel wire, 30 gauge, were attached for measurement of panel resistance and Seebeck voltage. Photographs of the components and of the completed panel are shown in Figure V-3.

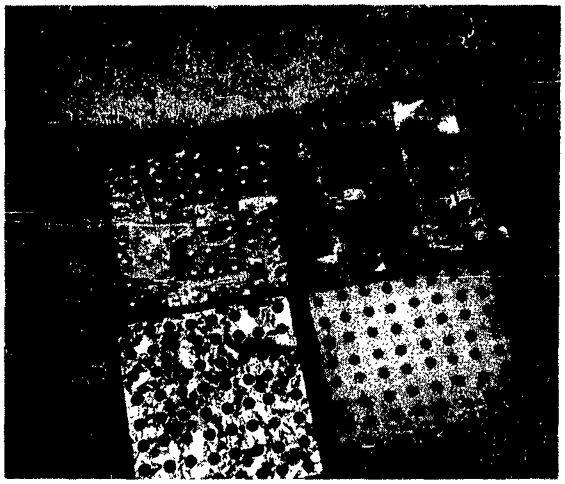
Prior to fabrication of the prototype panel using plastic foam (designated hereafter as F-1) a number of different types of foam of various densities were examined. Selection criteria were a) fabricability in the 1/16" thickness required, b) strength weight ratio and c) temperature capability. Initially, consideration was given to both foam-in-place and pre-foamed block systems. The use of foam-in-place systems was considered to pose a development problem better investigated only if positive merit was found in the use of foamed support structures. The foam finally selected for use (Eccofoam SH, 8 pounds per cubic foot) has adequate temp-



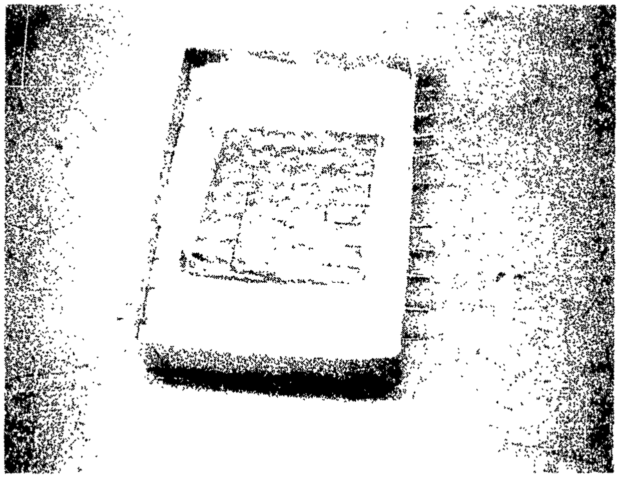
Solar Flat Plate Panel (no support structure)
and Vibration Table Mounting
Fixture

Fig. V-1


0.1"
.080"
.0001"



Plastic Foam Supported Panel
Components Ready For Final
Assembly



Finished Panel Ready for Testing

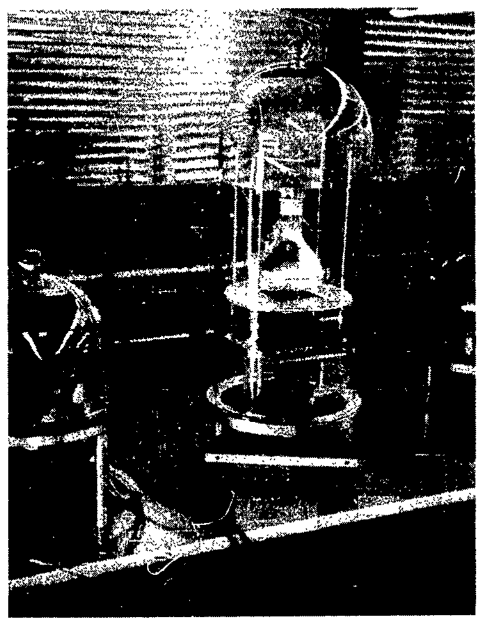
Figure V-3

erature capability, can readily be cut into a 1/16" thick section, and has a strength/weight ratio typical of the best foams available. At lower foam densities it was not possible to fabricate a section considered to have adequate strength.

An aluminum reflector sheet was cemented to the plastic foam and 0.220" diameter holes were drilled through to allow thermoelement assembly passage. The plastic foam was then cemented to the radiator plates. The cement was applied locally to minimize the weight of cement used and to avoid applying cement to those areas of the radiator plates where the thermoelement assemblies are bonded. The cement used was Emerson and Cuming Eccobond 45 LV.

The panel was then thermally shock tested in the cycling apparatus of Figure V-4. This apparatus is provided with a cooled (water or liquid nitrogen) cold sink and an infra-red lamp as a heat source. This test apparatus is suitable for panels up to 5" x 5" area. During thermal cycling the collector plate temperature varying between 450°F and 100°F and the radiator plate temperature between 260°F and 70°F. After a small number of cycles it was observed that the radiator plate and foam support structure were "bowing" in a manner concave with respect to the heat source. Figure V-5 is a photograph of this "bowing" in an early stage. Severe "buckling" of the collector plates also occurred and the combination of all these distortions resulted in thermoelement failure after about 20 thermal cycles. As became evident later, when the honeycomb panel was tested, oxidation and excessive temperature also contributed to the failures.

The failures occurred at the semiconductor to metal contacts, at the hot junction, at the metal to metal radiator bonds, and to a lesser extent at the metal to metal collector bonds.



Thermal Cycling Apparatus

Figure V-4

Plastic Foam Supported Panel In Thermal Cycling Apparatus Showing the Panel "Bowing"

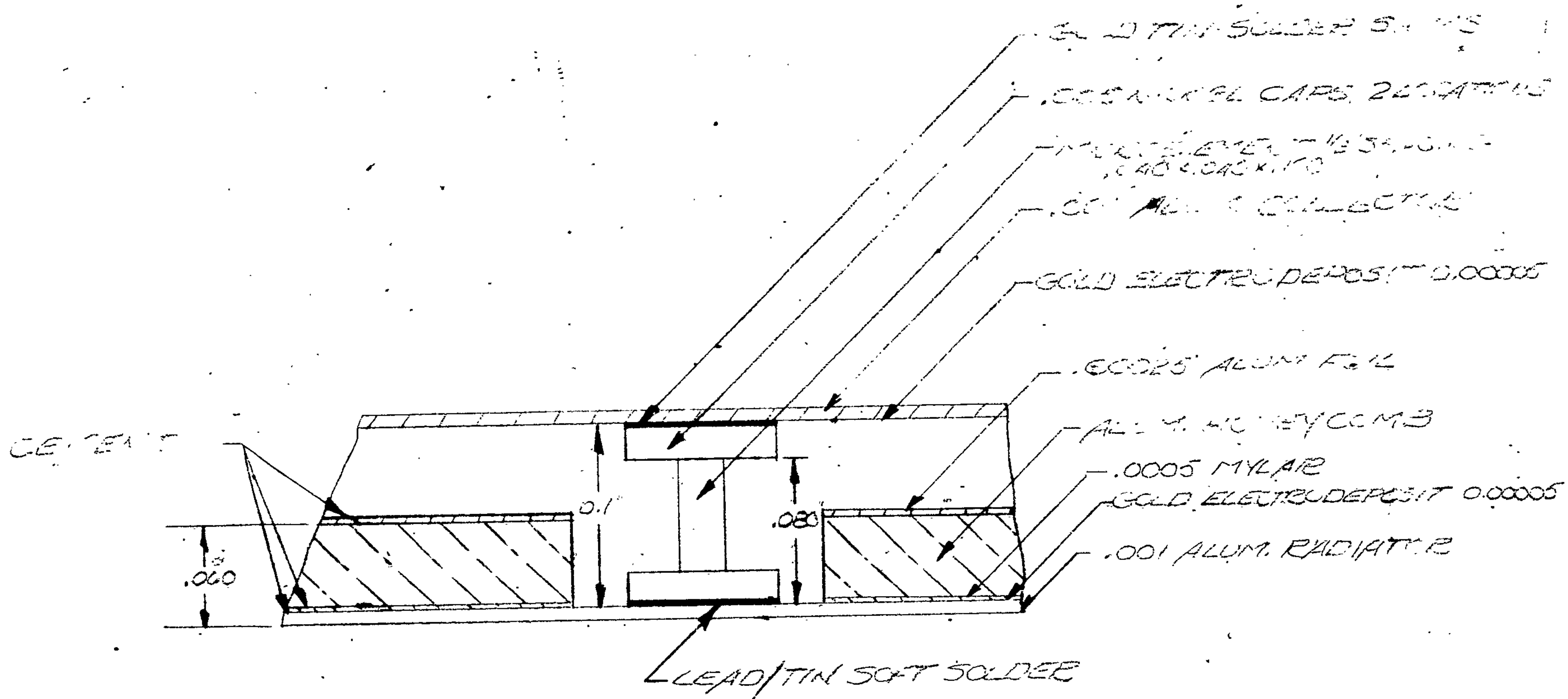
Figure V-5

The "bowing" of the radiator support structure was due to differences in thermal expansion between the plastic foam and the radiator sheet, the so-called "bimetal effect." This distortion was so severe as to cause this structural support concept to be eliminated from further consideration.

A 4" x 4" panel hereafter designated as H-1, was fabricated using an aluminum honeycomb (1/4" cell size 0.002" aluminum foil, 4.3 pounds per cubic foot, Hexcell Corporation) support structure. A schematic cross-section of this structure is given in Figure V-6 and weight data is given in Table V-1.

A mylar sheet, 0.005" thick, was used to electrically insulate the honeycomb from the radiator sheets. The assembly procedure for this panel was identical with that described for the F-1 panel with the following exceptions; Gold/tin solder was used exclusively for element to collector plate bonding, Biggs # 435 cement was used for honeycomb and mylar sheet attachment. Two of the four collector strips had stress relief slots similar to those described for the F-1 panel. After observing the test results of F-1, however, these stress relief slots were extended completely across the strip.

The H-1 panel was thermally cycled in a manner similar to the F-1 panel described above. In this test <u>no</u> distortion of the radiator plate or support structure was visually detectable. After only a few cycles, however, severe distortion of the collector sheets was observed. The strips without slots distorted as did the individual sections of the slotted strips. This distortion was accompanied by extensive thermoelement failure, again the dominant failure modes were the hot junction semiconductor to metal contacts and the cold junction bonds.



CROSS SECTION VIEW OF SOLAR FLAT PLATE CONVERTOR WITH ALUMINUM HONEYCOMB SUPPORT STRUCTURE

FIG. V-6

Examination of the failed components after completion of the test indicated some oxidation of the elements and contacts as well as evidence of excessive temperature in the central portion of the panel. The test apparatus has been modified to eliminate these problems.

The aluminum honeycomb support structure has sufficient merit to warrant further development. Another 4" x 4" panel using this support structure concept will be fabricated. The following modifications will be incorporated:

1. Radiator side metal to metal bonding will use a different solder than the lead/tin previously used, probably pure tin.
2. Tests are currently being conducted to determine an improved collector panel configuration to eliminate distortion upon heating. Various embossed patterns to "rigidize" the panels are being evaluated.

It is of interest at this point to discuss improvements that can be made in the weight analysis of Table V-1. One of the most serious weight factors is the solder used to connect the elements to their nickel caps. Future element assemblies incorporated into panels will use 0.090" diameter nickel caps instead of the 0.125" diameter presently used. This diameter change will not only reduce the weight of the caps themselves but should reduce the weight of the solder used. This change should result in a weight saving of about 10 grams per square foot.

The H-1 panel used 0.00005" gold electrodeposit instead of the 0.0001" gold used on F-1. This is a weight saving of almost 3 grams per square foot.

If a honeycomb supported panel can be made which passes all thermal shock, vibration, acceleration and shock tests, we plan to build a panel using 1.6 pounds per cubic foot honeycomb resulting in a weight reduction of 6 grams per square foot.

It is expected that development of improved techniques will allow a reduction of 1-2 grams per square foot in the amount of cement required and a reduction of 2-3 grams per square foot in the solder used for bonding the nickel caps to the aluminum sheets. This results in a reduced weight for a honeycomb supported panel of 54 grams per square foot. This is an optimistic prediction, a more realistic prediction would be 60 grams per square foot for the honeycomb panel.

A structural support design concept, different than those described above, is depicted in Figure V-7. A non-operating model of a 4" x 4" panel utilizing this concept is shown in photograph, Figure V-8. Preliminary procurement and experimentation leading to the fabrication of an operating model using this design concept has been started. Fabrication is expected to begin in the very near future.

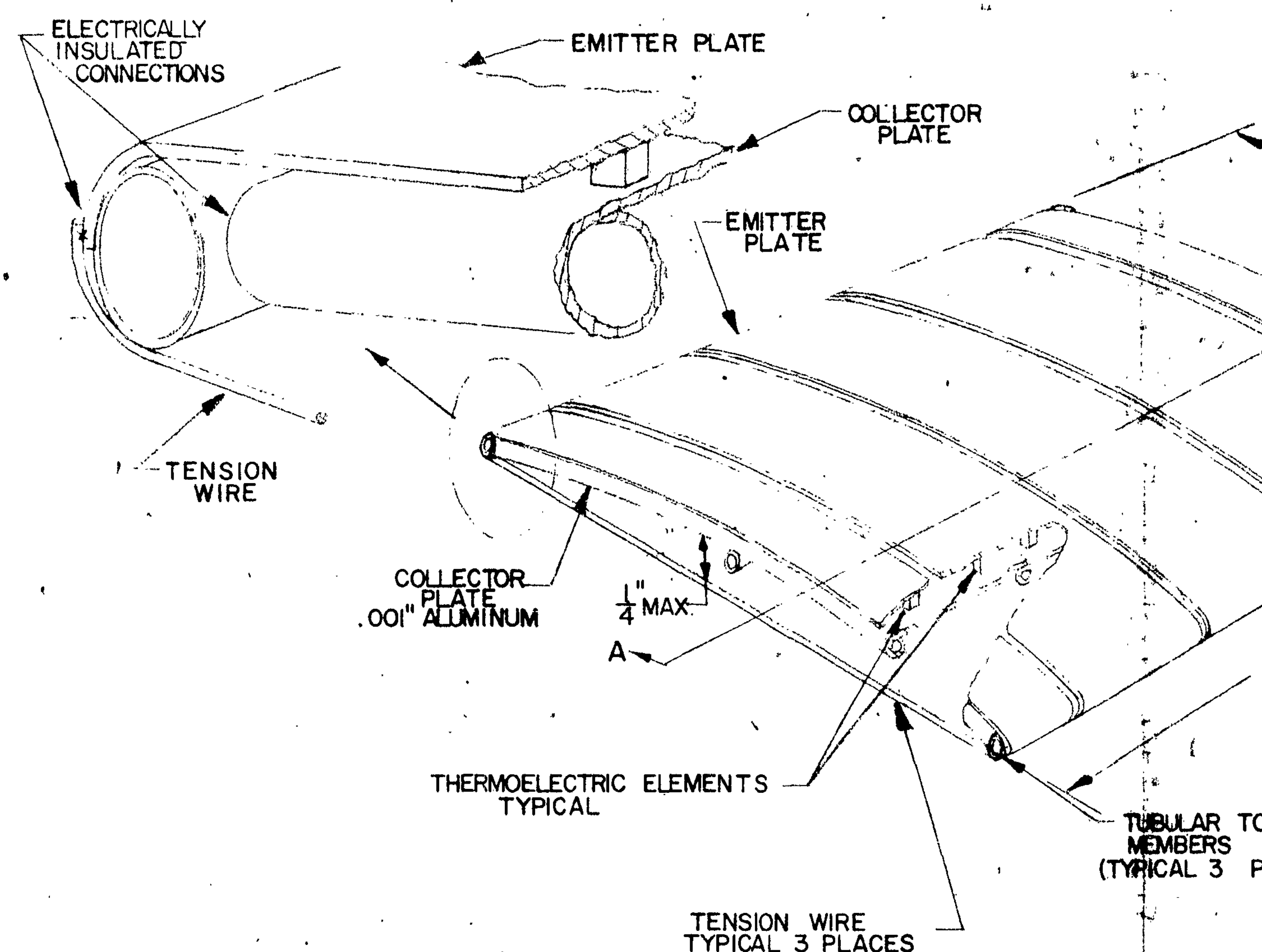


FIG. V-7

REVISIONS

1

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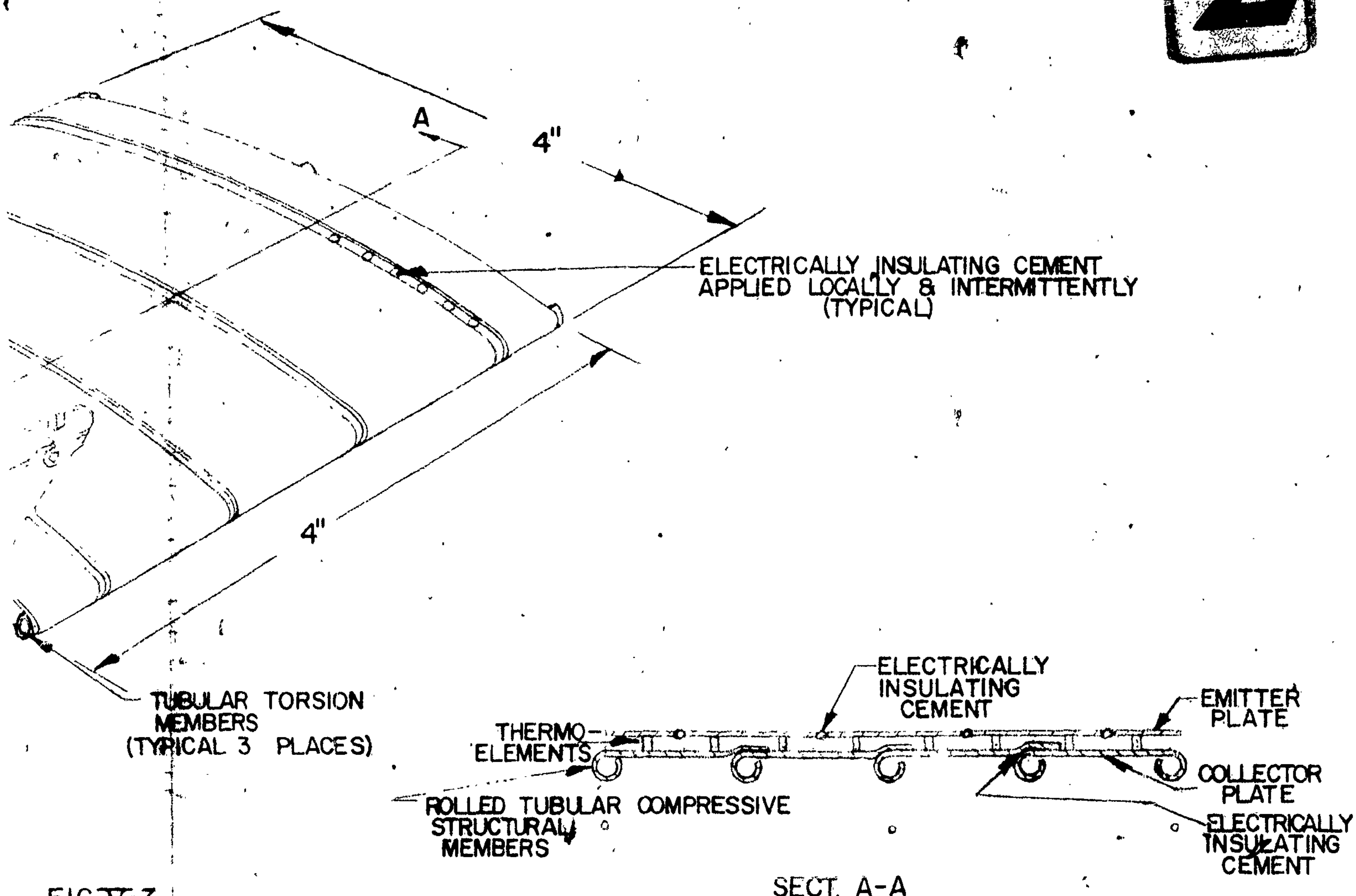
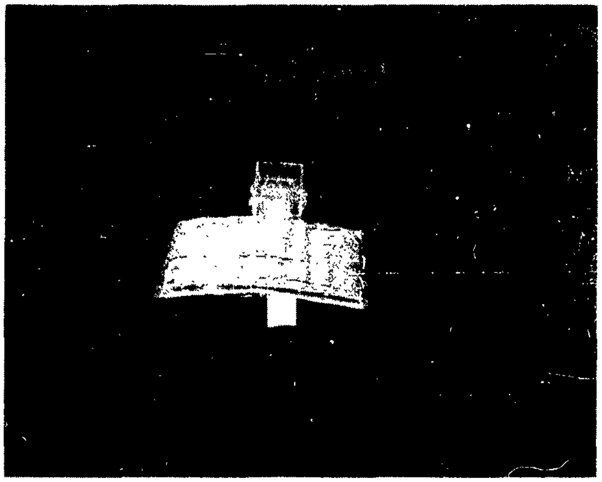


FIG. V-7

MATERIAL			SAMPLES OF THIS PART MUST BE SUBMITTED FOR APPROVAL TO ENGINEERING DEPT. BEFORE PROCEEDING WITH PRODUCTION.	GENERAL INSTRUMENT CORP. THERMOELECTRIC DIVISION 65 GOUVERNEUR ST. NEWARK, N. J.
FINISH			DESCRIPTION: PROPOSED RIGID DESIGN DESIGN-SOLAR FLAT PLATE GENERATOR	
TEMPER				
DIMENSIONAL TOLERANCES UNLESS OTHERWISE SPECIFIED				
FRAC.	DEC.	ANG.	DRAWN S.C. / DATE	NO. REQD. / SCALE
± 1/64	± .005	± 30'	CHECKED / DATE	DRAWING NUMBER / ISSUE
NEXT ASSY.			APPROVED / DATE	



Photograph of Non-Operating Model
of "Bowed" Flat Plate Structure

Figure V-8

TABLE V-1

WEIGHT ANALYSIS

of 4" x 4" Solar Flat Plate Panels

Using Plastic Foam and Aluminum Honeycomb

Support Structures

Component	F-1 Plastic Foam grams per 4" x 4"	F-1 Plastic Foam grams per sq. foot	H-1 Aluminum Honeycomb grams per 4" x 4"	H-1 Aluminum Honeycomb grams per sq. foot
P & N Thermo-elements, 1/2" centers	1.20	10.80	1.20	10.80
Nickel caps	0.40	3.60	0.40	3.60
Solder, nickel caps to thermoelements	1.92	17.28	1.92	17.28
Solder, bonding nickel caps to aluminum	.78	7.02	.78	7.02
Collector sheet aluminum	.72	6.48	.72	6.48
Radiator sheet aluminum	.72	6.48	.72	6.48
Gold plating	.64	5.76	.32	2.88
Aluminum reflector sheet	.17	1.63	0.17	1.63
Mylar sheet	--	--	0.19	1.66
Plastic foam	1.8	16.20	--	--
Aluminum honeycomb	--	--	1.35	10.65
Cement	.55	4.95	.70	6.30
Total	8.90	80.20	8.47	74.78

VI. THERMOELEMENT TO PLATE BONDING

A problem area uncovered on a previous program was in the attachment or bonding of nickel contacts on the thermocouple assemblies to gold plated aluminum collector and radiator sheets. These bonds must provide low thermal and electrical impedance pat... In the General Instrument design the collector bond must operate at 230°C and the radiator bond at 100°C. The bonds must be able to withstand thermal cycling, vibration, shock, etc.

As discussed in Section VI of this report, many failures during our thermal cycling tests were due to radiator side bonds and a few were due to collector side bonding.

The following solders have been considered for collector side bonding; 95% Pb/2.5%Ag/2.5% In, 80% Sn/20% Ag, Bi. The first two have been tested. The Sn/Ag solder is very simple to use but on some thermal cycling tests it appears to corrode the aluminum collector sheet resulting in failure. This is a result that could not be predicted from a study of binary phase diagrams. The Pb/Ag/In solder is more difficult to use but corrosion has not been observed to date. The bismuth solder has not been used because of the proximity of the melting point of bismuth, 271°C, to the operating temperature, 230°C.

The difficulty in collector side bonding, aside from metallurgical problems, lies in the fact that the melting point of the solder used for bonding is higher than the melting point of the solder used for metal-to-semiconductor joining. This problem does not exist at the radiator side because lower melting point solders can be used. Radiator side bonding is, however, complicated by the fact that the interfaces to be bonded are hidden from the view of the operator.

The appearance of failed collector and radiator bonds indicates that the primary cause of failure is the fact that the solder bonds were not made at a sufficiently high temperature. Recent samples of collector side bonds made at a higher temperature give indications of better results.

Most of the tests conducted to date have used a 60% Pb/40% Sn solder for radiator side bonding. A pure tin solder is of interest as it has higher strength at expected operating temperatures. Preliminary tests are encouraging.

VII. WORK PLANNED FOR THE NEXT QUARTER

The following items of work are programmed for the next quarter:

1. Prepare detailed test plan for testing prototype panels
2. Complete evaluation of candidate thermoelectric materials
3. Fabricate "Bowed" support structure, 4" x 4" panel for evaluation
4. Fabricate improved honeycomb supported 4" x 4" panel for evaluation
5. Investigate other support structure designs
6. Perform sublimation testing of thermoelectric materials
7. Investigation of thermal storage in solar flat plate panels.

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